Optically Active β-Naphthylphenylphosphine Oxide

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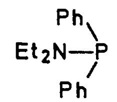
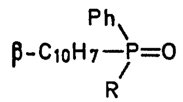
Summary The optically active secondary phosphine oxide β-naphthylphenylphosphine oxide has been prepared.

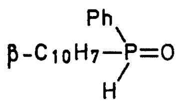
ALTHOUGH optically active trialkyl- or tertiary alkylarylphosphine oxides have been known for some time, an optically active secondary oxide, benzylphenylphosphine oxide, was first prepared only recently. We report the preparation of optically active β-naphthylphenylphosphine oxide.



(I)



(II)



(III)

Chlorodiethylaminophenylphosphine[2] [(I), b.p. 135—136°/10 mm Hg] was prepared from dichlorophenylphosphine[3] and diethylamine. Reaction of (I) with β-naphthylmagnesium bromide, followed by oxidation *in situ* (15% H_2O_2) and decomposition with 37%-HCl, gave β-naphthylphenylphosphinic acid [(II; R = OH), m.p. 164—166° (from EtOH) lit.[4] 165—166°]. A mixture of 0·17 mole of (II; R = OH) with 1·46 ml of thionyl chloride (1·5 hr., water bath) gave, after removal of the excess of thionyl chloride by distillation, β-naphthylphenylphosphinyl chloride [(II; R = Cl) b.p. 195—198°/0·05 mm Hg] (80·5%). This substance (0·105 mole) was heated (48 hr., water bath) with 0·105 mole of (—)-menthol and 0·125 mole of pyridine. After removal of pyridine hydrochloride and unchanged starting material, the filtrate, on standing for 12d., gave the less soluble diastereoisomer of (—)-menthyl β-naphthylphenylphosphinate [II; R = (—)-menthoxy]; m.p. 101—103° and $[\alpha]_D^{23}$ — 89·71 (*c* 0·0363, C_6H_6), after three recrystallisations from n-hexane. Reduction of [II; R = (—)-menthoxy] (10 mmole) with $LiAlH_4$ (20 mmole), followed by treatment with saturated NH_4Cl gave crude β-naphthylphenylphosphine oxide (III). Pure (III), after chromatography on silica gel and three recrystallisations from benzene–hexane (1 : 1), had m.p. 184—186° and $[\alpha]_D^{25}$ — 0·59° (*c* 0·476, $CHCl_3$). Although the observed rotation is low, several observations suggest that the activity must be due to the phosphine oxide itself. In a control experiment, it was found that racemic β-naphthylphenylphosphine oxide is clearly separated from both (—)-menthol and (—)-menthyl β-naphthylphenylphosphinate by the procedure used in isolating the optically active product. The optical active material racemizes readily in dilute MeOH–HCl or MeOH–MeONa; racemization of menthol or of a menthyl derivative under these conditions is highly unlikely.

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[1] T. L. Emmich and R. L. Letsinger, *J. Amer. Chem. Soc.*, 1968, **90**, 3459.

[2] H. Hoffmann, R. Grunewald, and L. Horner, *Chem. Ber.*, 1960, **93**, 861.

[3] B. Buchner and L. B. Lockahart jun., *Org. Synth.*, 1951, **31**, 88.

[4] O. Korpion, R. A. Lewis, J. Chickos, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4842.